PCT WORLD INTELLECTUAL Interna

INTERNATIONAL APPLICATION PUBLISHED U

WO 9602623A1

(51) International Patent Classification 6 : C11D 3/386 | A1

(43) International Publication Date: 1 February 1996 (01.02.96)

(21) International Application Number: PCT/EP95/02875

(22) International Filing Date: 18 July 1995 (18.07.95)

(30) Priority Data:
94202101.5 18 July 1994 (18.07.94) EP
(34) Countries for which the regional or international application was filed: NL et al.

(71) Applicant *(for all designated States except US)*: GENENCOR INTERNATIONAL INC. [US/US]; 4 Cambridge Place, 1870 South Winton Road, Rochester, NY 14618 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: VAN EE, Jan, Hendrik [NL/NL]; Brede Englaan 5, NL-1272 GR Huizen (NL). BOLLIER, Marc, P. [BE/BE]; Allée des Pommiers 2, B-4601 Argenteau (BE).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ENZYMATIC BLEACH BOOSTER COMPOSITIONS

(57) Abstract

This invention relates to an enzymatic bleach booster composition which provides bleaching activity using enzymes. The composition can be added to a washing or cleaning composition prior to the washing or cleaning procedure and will result in effective bleaching. By using the enzymatic bleach booster composition, the environmentally unwanted chemical bleach compositions can be replaced.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

ENZYMATIC BLEACH BOOSTER COMPOSITIONS

Field of the invention

The present invention relates to bleaching of textiles.

Background of the invention

In previous ages, most stubborn stains, e.g. fruit, red wine, coffee and tea, which could not be washed out from textiles, were oxidatively "removed" via grass bleaching i.e. spreading the washed fabrics on the lawn and exposing it for a longer time to bright sunlight. In the early 1900's this time consuming method was replaced by washing with a mixture of soda, silicate and perborate, thus allowing for one-step washing and bleaching. Over the years these prototype mixtures have evolved in rather complex formulations that may contain as many as 15 - 20 different ingredients which all have their specific tasks in textile cleaning. Volume-wise the most important ingredients are surfactants, builders and bleaches. The total world production of synthetic surfactants in 1992 amounted ± 4 million tons, for builders this was ± 4 million tons, and for bleaches this amounted to ± 2 million tons per annum. From these figures it is obvious that the natural resources needed to produce these volumes are really outrageous, and that, from an environmental burden point of view, these components are quite suspicious. Focussing on the biodegradability of bleaches the issues may be summarised as follows:

The two mostly used bleaches in detergents are chlorine bleach (sodium hypochlorite) and perborate (sodium perborate mono/tetra hydrate). Notably chlorine bleach is the most dangerous chemical that is being used in households. Use of chlorine may cause the synthesis of very poisoning organo-chloro compounds, such as trihalomethans (chloroform) and dioxines, which in general are also very hard to degrade. Also the use of perborate is growingly troublesome, because of the very large quantities that are currently being used, there is considerable accumulation (in the drinking water) of mineral boron, which cannot be degraded in the environment and cannot be removed from the water by sewage treatment installations. Boron is low poisoning for aquatic animals, but quite problematic for aquatic plants.

An extra negative for the use of perborate is that its bleaching activity at low temperatures is limited. As a consequence bleach activators, such as TAED (tetra acetyl ethylene diamine), are added. These activators are not needed in case percarbonate is being used as a bleaching agent. However percarbonate is not stable in detergents, unless EDTA (ethylene diamine tetra acetic acid) (significant quantities, non-biodegradable) as a stabiliser is added.

From this summary it is clear that not only the environmental bio burden, related to extremely large scale production levels of these ingredients are troublesome, but also their biodegradability is under continuous debate and worry, and that less environmentally harmful alternatives will be most welcomed.

As mentioned above, today an average heavy duty laundry detergent is composed of as many as 15 - 20 ingredients, chosen by the manufacturer to optimize the performance as much as (economically) possible, each ingredient having its own specific function. On a weight basis, surfactants, builders and bleaching components comprise the vast majority of these formulations. This is

basically due to their performance profile, which is typical for chemical activities i.e. at low concentrations a rather poor performance, at a certain concentration a dramatic increase in performance and beyond that concentration no significant increase in performance.

Bleaching components such as sodium perborate and percarbonate are also needed in high concentrations due to their chemical action mechanisms, which are dependent on the type of stain, the type of fabric, the temperature the pH and the concentration of specific bi-valent metal ions. For instance, the mechanism is strongly inhibited by lowering the wash temperature; from 80°C to 20°C the bleaching reaction kinetics are slowed down by a factor 1000. Instability of the bleaching agents, as a results of the presence of certain bi-valent metal ions is also an issue and reason to relatively overdose the bleach or to add chelaters such as EDTA or activators such as manganese porphyrins or manganese diols/polyols. An alternative to the activation of persalts is the in situ generation of peracids via bleach activators such as TAED, TAGU and SNOBS. This approach requires a relatively high pH and requires (again) stabilisers to prevent the formation of highly active radicals that may cause dye and fabric damage. All in all chemical bleaching is rather complex, does have limitations in terms of type of fabric and (low) temperature and pH applications, and is most certainly not free from risks concerning fabric color and fabric care.

Moreover, basically, bleaching is the destruction of chromophores in highly conjugated organic bio macro-molecules such as anthocyanins (fruit stains), tannins (tea stains) and chlorophyllins (grass stains) via oxidation of a number of double bonds in these molecules, which causes a shift in the absorption profiles of the chromophores from visible (on the fabric) to less visible or unvisible, (but still present) on the fabric. In other words the stains are not really being removed from the textile, but only seem to

be removed, because after oxidation they are no longer visible.

In contrast to chemical bleaching, bleaching processes that operate via an enzymatic mechanism are described.

But although enzymatic bleaching was already described in the early seventies (US 3640877), until now there are no detergent compositions comprising an enzymatic bleaching system. This will probably be due to the incompatibility of enzymatic bleach compositions with other detergent ingredients. The enzymes are not stable when formulated with other detergent ingredients.

Summary of the invention

It has been found that chemical bleach, in the application of bleaches in washing and cleaning procedures, can be substituted by an enzymatic bleach booster composition.

Accordingly, the present invention relates to enzymatic bleach booster compositions, which compositions are capable of exerting a bleaching effect on objects to be bleached, washed or cleaned. The enzymatic bleach booster compositions comprise at least an enzyme and a substrate for this enzyme, which substrate can be converted by the enzyme in a bleach active compound.

Another object of the invention is a method of bleaching, washing or cleaning a soiled object in which the method is characterized by the following steps:

a) supplying an enzymatic bleach booster composition and optionally a washing or cleaning composition to the soiled object; and

b) washing or cleaning the soiled object.

Still another object of the invention is a bleach protector composition, which is capable of increasing the effectiveness of bleach, when applied in laundry washing.

Detailed description of the invention

Enzymatic bleach booster compositions of the invention are compositions which mainly consist of an enzyme and a substrate for this enzyme, which substrate can be converted by the enzyme in a bleach active compound.

Contrary to prior art detergents comprising an enzymatic bleach system in which the enzymes are not stable, the enzymatic bleach booster compositions according to the invention comprise very little surfactants and/or builders.

The amount of surfactants and/or builders is preferably below 5%. In one embodiment of the invention the enzymatic bleach booster composition comprises no surfactants and/or builders at all.

Enzymes that could be used in enzymatic bleach booster compositions are for example oxidases, such as oxido-reductases and peroxidases. As a substrate for these enzymes short-chain alcohols, sugars etc. could be used. For example glucose oxidase, ribose oxidase, methanol oxidase or ethanol oxidase and their respective substrates glucose, ribose, methanol and ethanol could be used.

Bleach active compounds are for example hydrogen peroxide, peracids, etc.

Enzymatic bleach booster compositions of the invention may further comprise bleach activators. Bleach activators are substances which react with oxygen-molecules (originating) from persalts, to form bleach active peracids. Surprisingly, it has been found that the addition of bleach activators like TAED, TAGU (tetra acetyl glycol Uril), PAG (penta acetyl glucose), SNOBS (sodium nonaoyl oxibenzene sulphonate) and ISONOBS (sodium isononaoyl oxibenzene sulphonate) will result in a better performance.

Furthermore, enzymatic bleach booster compositions of the invention may comprise so-called bleach protectors. Bleach protectors are substances that protect the bleaching active compound from attack of bleach destroying substances. For example catalase which is present on laundry is able to degrade hydrogen peroxide rapidly, which will reduce the

bleaching effect of the bleaching composition. Incorporating substances like a bleach stable protease which will degrade the catalase, or hydroxyl ammonium sulphate, which inhibits the catalase, in the enzymatic bleach booster composition will protect the bleach from degradation.

Bleach protectors will increase the bleaching effectiveness of the enzymatic bleach booster composition.

Bleach protector compositions comprising a bleach stable protease and/or a catalase-inhibitor, like hydroxyl ammonium sulphate are also part of the invention. These compositions may be incorporated in the enzymatic bleach booster composition or may be used seperately. Bleach protector compositions which may comprise other enzymes (e.g. amylase, cellulase or lipase) are also capable of protecting chemical bleach.

The enzymatic bleach booster composition may further comprise, depending on the formulation type, minor quantities of e.g. processing aids and stabilisers.

This way of enzymatic bleaching has several advantages both in terms of cleaning capabilities as well as in terms of economic- and environmental issues. For instance it can be demonstrated that enzymes generate significant performance levels at rather moderate concentrations of typically 0.2 - 1.0 % on a weight basis, but fully substitute or even surpass the performance of current chemical cleaners (such as bleaching salts), at higher enzyme dosages viz: 1.0-5.0 % on a weight basis. This is found to be also true at moderate till low washing temperatures and in moderate till high water hardnesses. Apparently the use of enzymes in cleaning will facilitate the bleaching process thus avoiding the use of aggressive chemicals and costly high washing temperatures, demonstrating their specific cleaning benefits.

Also from a manufacturing point of view, the use of enzymes in bleaching is beneficial. Enzymes are being recovered from large scale fermentation of naturally occurring micro-organisms that produce these enzymes quite

effectively. Since these micro organisms are being grown on naturally occurring nutrients, such as organic nitrogen- and carbon sources, the bioburden, caused by the manufacturing of the raw materials is in comparison to that of chemicals negligibly low. Also the energy required for production of enzymatic bleach is extremely low relative to the chemical alternative (apprx. 25 MJ/kg vs 60 MJ/kg), which in the light of lowest possible resources consumption is clearly in favour of the enzymatic rather than the chemical product.

Because enzymes are being produced by naturally occurring micro-organisms, their origin is fully biological, and therefore their biodegradability is 100 %. This in contrast to the biodegradability of at least some chemical bleaching agents. From this comparison it is clear that the bio-burden of enzymatic bleaching is absolutely negligible, demonstrating their full environmental compatibility/ superiority over chemical alternatives.

Basically enzymes, to be used in the enzymatic bleach booster composition or bleach protector composition, are being produced by large scale fermentation of micro-organisms like bacteria, such as Baccilli, Streptomyces, Pseudomonas, or yeasts or fungi, etc. Typically the production is started by pumping in nutrients comprising sugars, proteins, salts, etc. into the fermenter (> 100 m^3), which is then (steam) sterilised at a temperature of approx. 120°C for several hours. Meanwhile a preculture of a selected micro-organism is prepared (small culture flask, containing broth, grown for 24-48 hours), which culture is used for inoculation of the fermenter, usually via a small fermenter as an intermediate step. In order to get optimal growth vigorous stirring is necessary to assure good nutrient distribution and good oxygen dissolution. This stirring and also as a result of nutrient consumption (combustion), the heat, which is released, is absorbed via cooling coils. During the fermentation (48-100 hours at approx. 40°C) several parameters are monitored to check pure microbial growth and enzyme production, and to automatically

adjust nutrient levels, oxygen uptake, pH, temperature, etc. After the fermentation, the broth is treated with chemicals and solvents to kill the production micro-organisms, filtered to remove germs and stored to cool down. With the aid of inorganic salts and organic solvents the enzyme is precipitated from the clear liquid, filtered and washed, dried and finally sieved. During all these processes the enzyme activity and purity is checked. Finally the enzyme is suitably formulated to liquids, slurries or (dust free) granulates. These granulates may be of the type to contain various types of enzymes in various overlayers to allow for so-called sequential release of the enzymes upon application.

Subsequently, or during enzyme formulation, an enzymatic bleach booster formulation can be produced by mixing a selection of enzymes and their substrates plus minor quantities of activator and/or stabiliser, processing aids etc, to be contained in a useful deliverance system such as a bottle, a sachet, an ampoule, a tablet or the like, depending on the physical appearance of the (concentrated) enzyme mixture.

Due to their nature enzymes act as biochemical catalysts i.ed. they facilitate a certain reaction drastically, without really being an active participant, which is being transformed or "consumed" by that reaction. By this invention it has been found, that upon application of enzymes, as the main ingredient in enzymatic bleach boosting processes, these enzymes apparently do act, and therefore give good performances, under moderate till very low temperatures, at which chemical bleaching usually is rather poor. Also in the absence of builders, which are normally necessary to constitute low water hardness conditions to allow sufficient performance of the chemical ingredients, it is found that enzymes do perform excellently. By this invention it is specifically demonstrated that in the absence of chemical bleach, sufficient bleaching activity can be obtained, provided the

proper enzyme mixture is being applied. Surprisingly it was also found that, in the absence of anti-redeposition agents and optical brighteners, with certain enzyme cocktails an unexpectedly high whiteness level of the fabrics can be reached. Apparently enzymes are particularly active and stable under application conditions to allow for the use of only moderate enzyme concentrations whilst still getting good performance results.

Another object of the invention is a method of bleaching, washing or cleaning a soiled object in which the method is characterized by the following steps:

a) supplying an enzymatic bleach booster composition and optionally a washing or cleaning composition to the soiled object; and

b) washing or cleaning the soiled object.

The soiled object can be anything that needs to be bleached, washed or cleaned. For example the soiled object can be laundry, china, glasses, kitchen or sanitary floors and so on. The soiled objects can be found in households, institutions (like hospitals) and in industrial environments.

The washing or cleaning composition may comprise a detergent composition (that is suitable for application in which it will be used). The enzymatic bleach booster composition is added to the washing or cleaning composition to provide a bleaching activity for the thus obtained composition.

The enzymatic bleach booster composition can also be used after dissolution in water or when it is formulated as a liquid, it could be used non-diluted.

A big advantage of the enzymatic bleach booster composition is that it can be dosed in an amount that is needed for the job to be done. Furthermore it can be used seperately, e.g. in the bleaching of white fabrics that appeared to have become yellowish.

The invention further relates to a broad field of applications, because the soils and stains that can be removed are quite universal.

Soils and stains may vary considerably in terms of their composition, most of them are fully natural due to the fact that they are derived after spillage of all kinds of natural substances such as for instance food and drinks, or are the results of contact with the body. Therefore most stains may considered to be a mixture of bio-macromolecules and other particular soil, most of the time significantly denatured and (therefore) firmly attached to the surface (fabric, dish, etc), and consequently very difficult to remove. By using enzymatic bleach booster compositions it is found that all kinds of natural occurring soils can be removed rather easily, even at low temperatures, most specifically stains that are sensitive to biochemical hydrolases, oxidases, and lyases. Surprisingly other soils are being removed concomitantly, giving an extremely white appearance of the enzymatically bleach boosted, washed textile or other surface. In other words it does not really matter where the soil and stain is coming from, nor where it is sitting. As long as sufficient quantities of bleach boosting enzymes plus stabilisers are present in the enzymatic bleach booster composition the removal of soil and stains will be carried out quite effectively, provided some mechanical force and some rinsing with water is carried out, either in typically designed equipment or by hand. Therefore the field of application may be the area of textile care and cleaning i.e. the field of household laundry cleaning in washing machines, or via manual cleaning. Another field of application may be the area of industrial and institutional cleaning as superior alternative for the rather aggressive chemical cleaning processes that are currently being applied. Another field of application may be the area of dry cleaning which is currently being performed with basically very versatile and therefore strongly air polluting chemicals. Again another field of application may be the

area of either ADD's (automatic dishwash detergents) or HDD's (hand dishwash detergents), as a better performing alternative, which is also more compatible with for instance delicate china or silver cutlery, due to its less aggressive nature, and therefore more friendly to the end-user i.e. the consumer as well as to the environment. Other examples of field of application are equipment cleaning, hardsurface cleaning, such as tiles, toiletbowls, and the like, which nowadays is done mainly via strong alkali, hypochlorite and hot water. It must be clear that all the area's described, are just some examples of fields of application of the current invention, and may not be considered as a limitation whatsoever.

As already mentioned in the previous section, one of the great advantages of enzymatic bleach boosting is that unexpected cleaning results can be obtained at relatively low enzyme concentrations and rather low washing temperatures. Washing at low enzyme concentrations, as compared to the rather high concentrations needed in chemical bleaching processes, will lead to significant savings in production energy/ environmental bio burden, for virtually the same cleaning results. For the sake of illustration; a change from washing at 60°C, (for proper chemical bleaching), to 40°C for excellent enzymatic bleaching, will save an amount of energy, that can be estimated to be approx. 0.5 kWh or 1800 kJ per wash. Therefore the energy spent on the production of an enzymatic bleach booster corresponds to less than 10 % of the energy savings by using these boosters (at low wash temperature).

From a biodegradability point of view, it may be stated, that enzymes are fully biodegradable and do not form an environmental risk, whatsoever. Over the last 15 years large quantities of enzymes have been produced and used as additives in a wide variety of applications, without any adverse effects on the health of the end-users, and/or the environment, and in this respect most certainly are better

alternatives for many chemicals, that currently are being used.

Another benefit of the use of enzymatic bleach booster compositions is that the enzymes contained in these compositions generate their bleaching activity in situ, which means at the place and time needed, rather than having the bleach already available in the dry (synthetic) detergent matrix, which asks for extra stability measures upon manufacturing, packaging and storage of the detergents.

All in all it can be said that the use of enzymatic bleach booster compositions is a better alternative relative to chemical bleaching in terms of: better performance, better for the environment, and with better economic results (lower production and application energy).

Examples

A test system for the enzymatic bleach booster composition was developed. This test system was based on the ability of the compositions to remove stains from either indicator swatches (e.g. commercially available swatches from EMPA (Swiss federal laboratories for materials testing & research, St. Gallen, Switzerland)) or household worn textiles, which were washed in a Miele type washing machine (W701) under fully controlled conditions. The performance of the enzymes was conveniently determined by reflectance measurements (on the textiles) which is well known to those skilled in the art.

In some cases the results of the washing experiments were evaluated through a panel evaluation in which individuals had to judge the results visually.

Example 1

As mentioned before, conventional powder detergents do contain either perborate or percarbonate as the most important bleaching agent. A drawback of conventional chemical bleaching is that its efficiency is significantly

slowed down at low temperatures e.g. at 40°C and lower, due to the rather poor solubility of the chemical bleaching system. In order to overcome this inefficiency, we successfully designed an enzymatic alternative, which is a combination of a suitable enzyme, a suitable substrate and an activator. As a typical example, which should not be considered as a limitation of the invention, of such an enzymatic bleach booster composition, we disclose the results obtained with: glucose oxidase (as the bleaching enzyme), glucose (as the substrate) and TAED (as the activator).

Test conditions:
Washing at 50, 40 and 30°C for 30 min.
Test swatches: A) Red wine on cotton (EMPA art.nr. 114)
B) Blood on cotton (EMPA art.nr. 111)

Results (% soil removal):
The % soil removal was calculated from the reflectance measurements, using the following formula:

$$\% \text{ soil removal} = \frac{R_{\text{soiled, and washed}} - R_{\text{soiled, not washed}}}{R_{\text{not soiled}} - R_{\text{soiled, not washed}}} * 100\%$$

(R denoting the reflectance)

	50°C		40°C		30°C	
	A	B	A	B	A	B
Detergent	37	80	37	79	30	76
Detergent + PB4	60	73	52	71	34	72
Detergent + PB4 + TAED	81	72	75	72	52	74
Detergent + GOX	43	81	39	80	49	79
Detergent + GOX + TAED	70	85	67	86	65	84

Detergent = IEC (zeolite containing test detergent obtained from WFK Krefeld, Germany) detergent without bleach : 5 g/l sud

PB4 = sodium perborate tetra hydrate : 12 % (w/w)

TAED = tetra acetyl ethylene diamine: 2% (w/w)

GOX = Glucose/Glucose oxidase (1:1) : 5% (w/w)

MAXAZYME GO® glucose oxidase (purchased from Gist-Brocades B.V.) with 2500 Sarrett Units/g was used.

From these results it is clear that the enzymatic bleach booster composition, specifically at low temperatures, performs better than current days chemical bleach compositions. Surprisingly this performance is significantly enhanced by the addition of TAED. Apparently the best low temperature bleaching activity can be obtained by a mixture of enzymes, substrates and an activator.

Example 2

One reason for rapid degradation of bleach activity is supposed to be the potential presence of e.g. catalases in textiles. These catalases are secreted by the human body upon perspiration and therefore are most commonly present in heavily worn socks, sport shirts and bedsheets. In order to overcome this bleach degradation, we have successfully designed specific enzyme mixtures comprising suitable proteolytic enzymes in combination with suitable stabilisers, able to suppress catalase activity released from the textile and therefore able to significantly boost the bleaching capacity. As a typical example, which should not be considered as a limitation of the invention, of such a bleach protector composition, we disclose the results obtained with MAXAPEM® CX20-protease, with 20 Maxapem Units/g, (as the bleach stable proteolytic enzyme obtainable from Genencor International Inc.) and hydroxylammonium-sulphate.

Test conditions:
Washing at 40°C
Test swatches: A) Red wine on cotton (EMPA ART. NR 114)
B) Blood on cotton (EMPA ART. NR 111)
C) Cocoa on cotton (EMPA ART. NR 112)

Results (% soil removal):

	A	B	C
Det + PB4 + TAED	100(*)	100(*)	100(*)
Det + PB4 + TAED + socks	62	80	46
Det + PB4 + TAED + socks + Mix	85	100	91

Det = IEC detergent without bleach : 5 g/l sud
PB4 = sodium perborate tetra hydrate : 12 % (w/w)
TAED = tetra acetyl ethylene diamine : 2 % (w/w)
Mix = MAXAPEM® protease/hydroxylammoniumsulphate (2:1) : 3 % (w/w)
(*) = set at 100 by definition

The above presented results show that the mixture of MAXAPEM® protease/hydroxyl ammonium sulphate restore most of the bleaching capacity of chemical bleach.

Example 3

Based on the results described in the previous two examples we have also tested the outcome of combinations of the enzymatic bleach booster composition and the bleach protector composition.

Testconditions:
Washing at 30 and 40°C
Test swatches: A) Red wine on cotton (EMPA ART. NR 114)
B) Blood on cotton (EMPA ART.NR 111)
Results (% soil removal):

	40°C		30°C	
	A	B	A	B
Det + PB4 + TAED	74	73	50	72
Det + PB4 + TAED + socks	44	58	31	58
Det + PB4 + TAED + socks + mix	63	74	42	73
Det + GOX + TAED + socks	42	60	47	55
Det + GOX + TAED + socks + mix	61	90	66	92

Det = IEC detergent without bleach : 5 g/l sud
PB4 = sodium perborate tetra hydrate : 12% (w/w)
TAED = tetra acetyl ethylene diamine: 2% (w/w)
Mix = MAXAPEM® protease/hydroxylammoniumsulphate (2:1) : 3% (w/w)
GOX = Glucose/MAXAZYME GO® Glucose oxidase (2500 SU/g) (1:1): 5% (w/w)

Surprisingly, since it was expected that the glucose oxidase would be affected by the protease, we found that the combination of GOX (Glucose/Glucose oxidase) and the protease containing bleach protector composition resulted in the best bleaching performance, especially at low temperatures.

Example 4

Alternatively we checked the results of the bleach protector composition by a panel analysis. For that reason a random selection was made amongst sufficient families to compose a group of 125 families, which was very heterogenous in washing habits, 80% of them having children, of which 50 % being younger than 12 years old. The group was asked to run house-hold washings for 3 periods of 3 weeks each, with the detergents the family was familiar with (test sample A), this detergent plus a bleach protector composition (test sample B) and this detergent plus a placebo (test sample C).

The bleach protector composition (dosed per wash) consisted of bleach stable MAXAPEM® CX 20 protease prills (20 Maxapem U/g) (purchased from Genencor International Inc.): 1.0 g
MAXAMYL® CXT 5000 amylase prills (5000 TAU/g) (purchased from Genencor International Inc.) : 0.4 g
and hydroxylammoniumsulphate crystals: 0.5 g
The placebo consisted of empty prills.

Based on a total of about 4000 house-hold washes, the results read as follows:

Preference;		
Test sample	A	21%
Test sample	B	54%
Test sample	C	22%
No difference		3%

Looking in more detail at the cleaning power, on a scale ranging from 1 = excellent, 2 = good, 3 = fair and 4 = bad, the results read as follows:

	Whiteness	Dirt removal	Overall
Test sample A	3.10	2.09	2.58
Test sample B	1.39	1.70	1.57
Test sample C	3.23	2.51	2.88

From these results it is clear that the addition of a bleach protector composition will boost up general detergency (best score in dirt removal), and surprisingly has also an enormous beneficial effect on fabric whiteness (best score on whiteness), which may be considered as a unexpected bonus, that allows for the reduction in use of optical brighteners.

Claims

1. An enzymatic bleach booster composition comprising at least

an enzyme and a substrate for this enzyme, which substrate can be converted by this enzyme in a bleach active compound.

2. An enzymatic bleach booster composition according to claim 1, which comprises very little builders and surfactants.

3. An enzymatic bleach booster composition according to claim 1 or 2, which further comprises a bleach activator.

4. An enzymatic bleach booster composition according to claim 1-3, which further comprises a bleach protector composition.

5. An enzymatic bleach booster composition according to claims 1-4, in which the enzyme is selected from glucose oxidase, ribose oxidase, methanol oxidase or ethanol oxidase.

6. An enzymatic bleach booster composition according to claim 1-4 in which the substrate is selected from glucose, ribose, methanol or ethanol.

7. An enzymatic bleach booster composition according to claim 3, in which the bleach activator is selected from TAED, TAGU, SNOBS, ISONOBS or PAG.

8. An enzymatic bleach booster composition according to claim 4, in which the bleach protector composition comprises a protease and/or a catalase inhibitor.

9. An enzymatic bleach booster composition according to claim 8 in which the catalase inhibitor is hydroxyl ammonium sulphate.

10. A method of bleaching, washing or cleaning a soiled object in which the method is characterized by the following steps:

a) supplying an enzymatic bleach booster composition and optionally a washing or cleaning composition to the soiled object; and

b) washing or cleaning the soiled object.

11. A method according to claim 10 in which the enzymatic bleach booster composition is defined in one of claims 1-9.

12. Use of a bleach protector composition capable of increasing the effectiveness of bleach in bleaching, washing or cleaning processes.

13. Use of a bleach protector composition according to claim 12, in which the bleach is obtained from an enzymatic bleach booster composition.

14. Use of a bleach activator capable of increasing the bleaching, washing or cleaning performance of enzymactic bleach booster compositions.

15. A bleach protector composition capable of increasing the effectiveness of bleach in bleaching, washing or cleaning processes which composition comprises a protease and hydroxylammonium sulphate.

INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/EP 95/02875

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 072 098 (UNILEVER PLC ET AL.) 16 February 1983 see page 2, line 31 - line 37 see page 3, line 1 - line 8 see page 14, line 34 - line 36 see page 15, line 1 - line 21 see page 18, line 30 - line 36 see claims 1-25	1-3,5-7, 10,11,14
Y	---	4,8,9,12
Y	DE,A,42 31 767 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 24 March 1994 see page 2, line 66 - line 68 see page 3, line 1 - line 2 see claims 1-3	4,8,9,12

	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 November 1995	24 -11- 1995

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Pelli Wablat, B

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/02875

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DATABASE WPI Week 9505, Derwent Publications Ltd., London, GB; AN 95-032534 & JP,A,6 315 907 (AMANO PHARM KK ET AL.) 15 November 1994 see abstract	1,2,5,6, 10,11
P,X	DATABASE WPI Week 9523, Derwent Publications Ltd., London, GB; AN 95-175511 & JP,A,7 097 597 (SEKISUI CHEM IND CO LTD) 11 April 1995 see abstract	1,2,5,6, 10,11
X	DATABASE WPI Week 8915, Derwent Publications Ltd., London, GB; AN 89-112334 & JP,A,1 060 693 (AMANO PHARM KK) 7 March 1989 see abstract	1,5,6
Y	RESEARCH DISCLOSURE, vol.292, no.62, August 1988 page 615 ANONYMOUS	1
Y	US,A,3 640 877 (M.R.R.GOBERT) 8 February 1972 cited in the application see claims	1
P,A	WO,A,95 07972 (UNILEVER NV ET AL.) 23 March 1995 see claims	1-15

INTERNATIONAL SEARCH REPORT

Inter al Application No
PCT/EP 95/02875

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0072098	16-02-83	AU-B-	548286	05-12-85
		AU-B-	8561682	12-01-84
		CA-A-	1184860	02-04-85
		GB-A,B	2101167	12-01-83
		JP-C-	1349868	28-11-86
		JP-A-	58017200	01-02-83
		JP-B-	61016318	30-04-86
		US-A-	4421668	20-12-83
DE-A-4231767	24-03-94	NONE		
US-A-3640877	08-02-72	NONE		
WO-A-9507972	23-03-95	AU-B-	7695594	03-04-95